

International Conference on Technologies and Materials for Renewable Energy, Environment and Sustainability, TMREES15

## Desulfurization of gas oil using a solar photocatalytic microreactor

*Mohammad Fadhil Abid*

*Chemical Engineering Department, University of Technology, Baghdad, Iraq*

*Emails: [dr\\_mfa@uotechnology.edu.iq](mailto:dr_mfa@uotechnology.edu.iq); [doctormfa@gmail.com](mailto:doctormfa@gmail.com)*

---

### Abstract

The desulfurization of dibenzothiophene (DBT) was studied in a homemade Y-shape catalytic microreactor utilizing solar incident energy. The microchannel was coated with TiO<sub>2</sub> nanoparticles. Performance of the microreactor was investigated using different conditions (e.g., DBT concentration, LHSV, operating temperature, and (H<sub>2</sub>O<sub>2</sub>/DBT) ratio). Our experiments show that, in the absence of UV light, no reaction takes place. The results revealed that outlet concentration of DBT decreases as the mean residence time in the microreactor increases. Also, it was noted that operating temperature has a positive impact on the degradation rate of DBT while LHSV showed a different image. The results reported an optimum (H<sub>2</sub>O<sub>2</sub>/DBT) ratio which gave maximum conversion of DBT. Kinetic study was carried out which confirmed that desulfurization of DBT followed a pseudo-first order reaction at 30 and 50°C, respectively. However deviation from linearity was observed at 60°C. Comparison between microreactor's performance and performance of batch reactors from published literature were illustrated. The Comparison confirmed the unique characteristics of the microreactor.

© 2015 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

Peer-review under responsibility of the Euro-Mediterranean Institute for Sustainable Development (EUMISD)

**Keywords:** Solar photocatalysis, desulfurization, gas oil, microreactor, Dibenzothiophene

---

Correspondence to: Dr. Mohammad F. Abid, email: [dr\\_mfa@uotechnology.edu.iq](mailto:dr_mfa@uotechnology.edu.iq), Mob. No: +9647709229217

## 1. Introduction

Crude oil is the largest and most widely used source of energy in the world. Major portions of the crude oils are used as transportation fuels such as gasoline, diesel and jet fuel. However, such crudes contain sulfur, typically in the form of organic sulfur compounds. The sulfur content and the API gravity are two properties which have a great influence on the value of the crude oil. The sulfur content is expressed as a percentage of sulfur by weight and varies from less than 0.1% to greater than 5% depending on the type and source of crude oils (Fadhel, 2010)[1]. Combustion of gasoil and diesel fuel source of crude oils (Fadhel, 2010)[1]. Combustion of gasoil and diesel fuel has been identified as one of the major emission sources of polyaromatic hydrocarbons (PAH) in urban areas. As environmental consciousness rises, all countries worldwide introduce more stringent legislation to limit the PAH content of diesel fuels. In the foreseeable future, a sulfur content as low as 10 ppm and a PAH content not greater than 2% may be proposed in most countries worldwide. Furthermore, the sulfur compounds are taken into account as the components of PAH. Dibenzothiophene (DBT) and its derivatives are the major sulfur species in diesel and gas oil. (Chen et al, 2010)[2]. Currently, hydrodesulfurization (HDS) is used to remove sulfur from hydrocarbons in petroleum refineries which require either increasing reactor residence time, or carrying out reactions in severe conditions (Al-Malki, 2004)[3]. The catalysts used in HDS are not active in removing refractory sulfur compounds, such as dibenzothiophenes (DBTs) and its derivatives, and these compounds require higher hydrogen consumption in the HDS process (Fadhel, 2010)[1].

In the past few years, microreactor technology is presented as a novel and breakthrough technology on which the new concept of production and research will be built upon. The chemical industry, biotechnology, pharmaceutical industry and medicine, life science, clinical and environmental diagnostic are just some of the small fields where this new concept in production, analysis and research could find its place of application (Šalić, 2012)[4]. By decreasing the equipment size by several magnitude levels, substantial economical benefits, improvement of intrinsic safety, and a reduction of environmental impact can be achieved (Rebrov et al. 2003)[5]. The large surface area, per volume, gives high thermal conductivity to a micro-channel allowing quick and accurate temperature control of the chemicals inside (Kusakabe, 2002)[6]. Recent reports have demonstrated that a vast range of organic reactions - including the aldol reaction (Wiles et al, 2001)[7], the synthesis of esters (Wiles et al., 2003)[8], the Hantzsch synthesis (Garcia-Egido et al., 2001)[9], and fluorinations (Hideki et al., 2013)[10], chlorination (Matsubara, 2011)[11] and brominating (Holger, 2005)[12] - can be performed within microreactors. Microreactors can be prepared from metal, glass, and a range of polymeric materials (Wang and Holladay, 2003)[13]. A number of techniques may be used to create the required network of microchannel, including photolithographic, molding, embossing and milling processes (Yuan-Chien et al, 2006) [14].

In the field of bio-catalysis, Drott et al. [15] have investigated the use of porous silicon as a carrier matrix in microstructured enzyme reactors, increasing the surface area onto which enzymes could be coupled, using the microreactor fabricated at 50 mA/cm<sup>2</sup> current density, they found that the enzyme activity was increased 100-fold compared with the reference reactor. Chambers et al., 1999 [16] have reported the development of a microreactor in

which elemental fluorine has been used to allow both the selective fluorination and perfluorination of organic compounds in a simple controllable manner. The synthesis of fluorine-containing organic compounds has many inherent safety issues such as safe handling and temperature control. (Chambers et al., 1999) outlined the potential benefits of the microreactor used as being ( i ) a small inventory of fluorine in the reaction zone, ( ii ) an opportunity for good mixing and temperature control and ( iii ) simple reaction scale-up. (Kelly et al., 2002)[17] developed a system of a microreactor in combination with a micro fuel cell as an alternative to conventional portable sources of electricity such as batteries due its ability to provide an uninterrupted supply of electricity as long as a supply of methanol and water can be provided. They proved that the energy storage density per unit volume/weight of this system was higher than that of batteries, which translates into less frequent recharging through the refilling of methanol fuel. The large surface area, per volume, gives high thermal conductivity to a micro-channel allowing quick and accurate temperature control of the chemicals inside[6] (Kusakabe, 2002). There are a lot of chemical systems using micro-channels. Many of them are made of transparent material, such as glass, plastics, or silicone rubber, so the researchers can visually observe the reactions [18-19] (Fujinami, 1998; Ooi, 2002).

The desulfurization reaction is most often considered as a pseudo 1<sup>st</sup> order rate reaction [20] (Arantegui et al., 1995). The pseudo 1<sup>st</sup> order approximation is associated with the overall degradation reaction of dibenzothiophene which may be assumed to consist of the following steps [20],

activation of substrate:



activation of oxidant:



substrate conversion with activated oxidant:



where T and  $h\nu$  represent the organic substrate and UV photon energy, respectively..

In the above degradation pathway, all the radicals formed by the collision of one photon and one molecule of  $H_2O_2$  are included in the term  $H_2O_2^*$ .  $H_2O_2$  itself does not oxidize DBT in the absence of UV light; but it helps the excited DBT molecules to be oxidized [21] (Hirai et al., 1997).

The aim of the present work was to investigate the desulfurization of gas oil utilizing a solar photocatalysis microreaction process. Influence of the operating variables such as initial sulfur content, inlet mixture flow rate, and  $H_2O_2$  loadings on reactor performance was investigated. In addition, the kinetic parameters of the desulfurization process were estimated.

## 1. Materials and Methods

### 1.1 Materials

The chemicals which have been used in this work are: Titanium dioxide ( $TiO_2$ , 80% anatasa) of Size (5-30nm) (specific surface area  $60 \pm 15 \text{ m}^2/\text{g}$  (BET), was obtained from Zhengzhou Xinyue Chemical Co., China.).

Dibenzothiophene (purity 97%, from Riedel-de Haën AG, Germany) was used as a model for the sulfur containing compounds in the fuel. N-hexane (purity 85%) was used as a carrying medium inside the microreactor for dibenzothiophene. N-Hexane was obtained from Merck Millipore, Malaysia. Deionized water and acetonitrile from LabScan- Poland were used as a mobile phase in the HPLC. The mobile phase prepared from (70% acetonitrile, 30% water). The hydrogen peroxide solution which is used as the oxidizing agent (purity 35%) was obtained from Merck-Gruppe, Germany. Ethanol used as storing solution for the windows (purity 95%, 190 PROOF, USP). Ethanol was obtained from Merck Inc. All chemicals are HPLC grade and were used as received without further purification.

## 2.2 Microreactor design and fabrication

For the design of a micro reactor, it has to be considered that both heat and mass transport time-scales are strongly correlated with the characteristic dimensions of the microreactor according to diffusion theory [22-23] (Wegeng et al., 1996; Branebjerg et al., 1996):

$$\text{Heat transport: } t \sim l^2/a \sim L/u \quad (4)$$

$$\text{Mass transport: } t \sim l^2/D \sim L/u \quad (5)$$

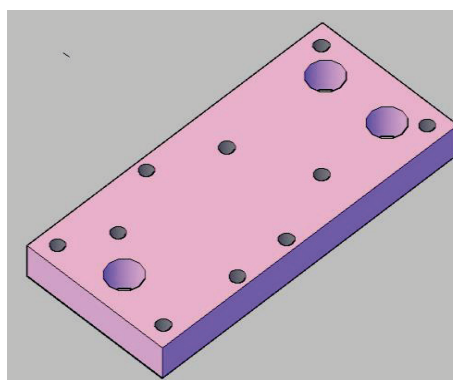
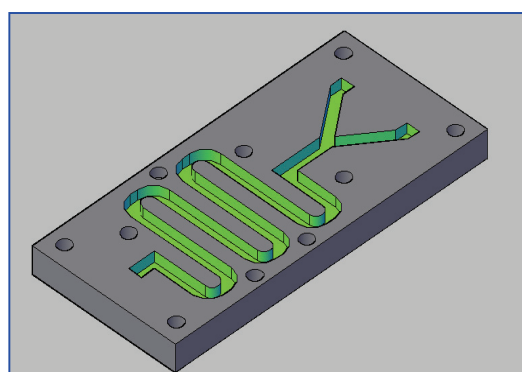
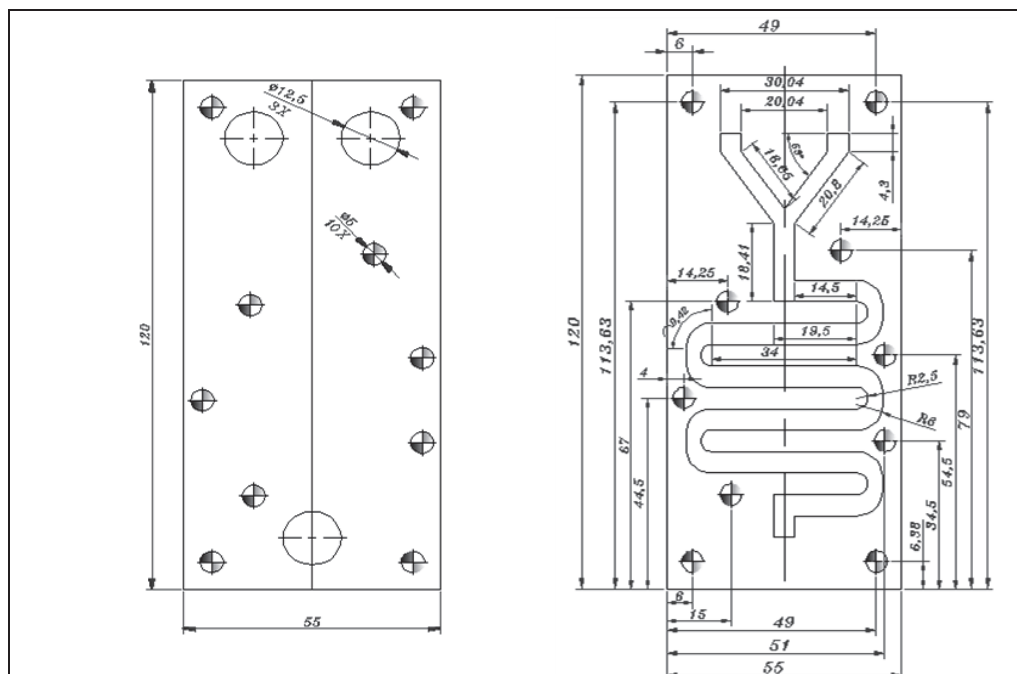
$$l^2/a \cdot t = l^2 \cdot u / a \cdot L \sim 1 \quad (6)$$

$$l^2/D \cdot t = l^2 \cdot u / D \cdot L \sim 1 \quad (7)$$

where

$L$ : travelling length,  $t$ : time-scale,  $l$ : diffusion length,  $a$ : thermal diffusivity of fluid,  $D$ : mass diffusivity,  $u$ : flow speed  
A Y-shape microreactor was designed and fabricated using 2D AUTOCAD software. The schematic diagram shown in Fig. 1 displays the dimensions of the reactor pattern. This reactor design has the advantage of independent control and monitoring of the reactant and product streams. It also provides in situ mixing of reactants, thus avoiding some of the hazards associated with a premixed feed. The mixing efficiency of the Y-junction depends on flow rates, nature of the reactant molecules and channel aspect ratio (width/height). This means that the mixing length can vary depending on reaction and operating conditions, but it is generally small [24] (Yeong, et al., 2000).

Fig. 2 shows the microreactor which was fabricated in the Workshop Training Centre-University of Technology. The upper and lower parts of the reactor were made of transparent elastic polydimethylsiloxane (PDMS) and aluminum alloy, respectively. A transparent flexible gasket was inserted between the two parts before bolted with each other.



(b) (a)

Figure 2 Disassembly of the microreactor (a) upper part, (b) lower part

### 2.3 Catalyst

Deposition of nano-TiO<sub>2</sub> particles on microchannel of the aluminum plate, in the present research was performed as follows:

1. In a beaker, 1.5 mL of a dilute nitric acid solution (pH = 3.5) and 4.5 mL of ethanol and 0.5 g nano-TiO<sub>2</sub> powder were added while stirring.
2. After a minute of stirring, a given volume suspension was carefully injected in the microchannel using a 5-ml

syringe. The suspension filled the microchannel and allowed to dry at 60°C for six hours.

3. The coated sample was then annealed for 30 minutes at 350°C.

4- This deposition process could be carried several times in succession so as to increase the total thickness. SEM was used to scan the effect of successive coating on microchannel as shown in Figure 4. The first coat does not cover the entire surface but additional coats lead to a complete coverage.

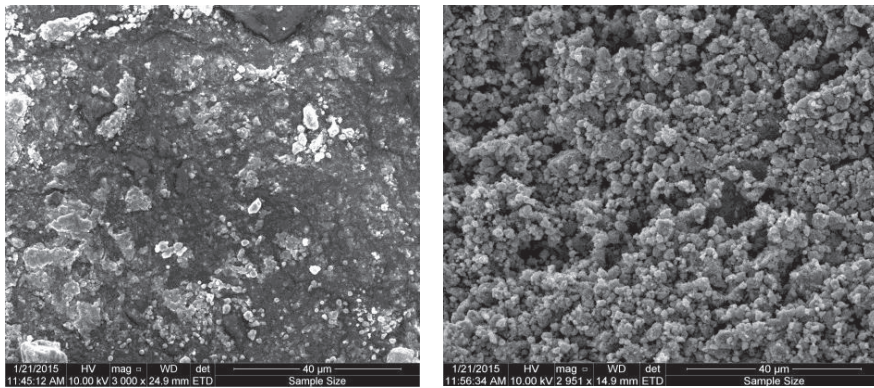


Figure 3: Effect of successive coating of microchannel with nanoTiO<sub>2</sub>, after first coating (left) and after third coating (right)

#### 2.4 Experimental setup

Fig. 4 presents a schematic diagram and a photographic view of the experimental setup is shown in Fig.5 (a, and b).

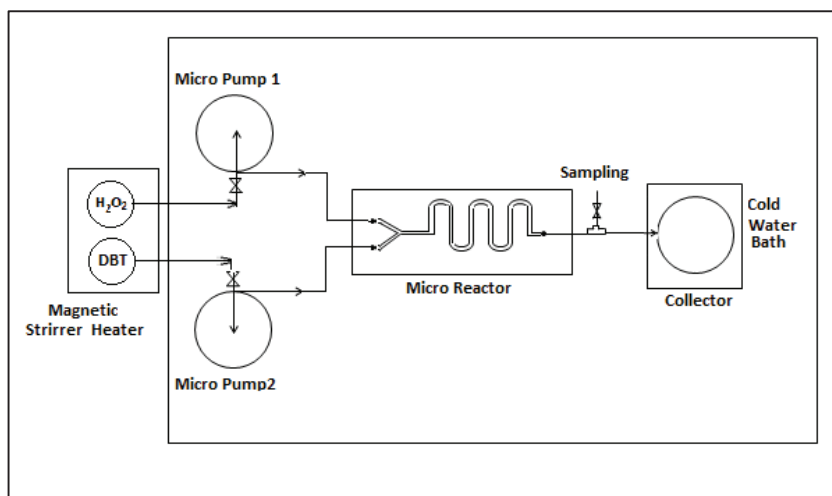


Figure 4 Schematic of the experimental setup

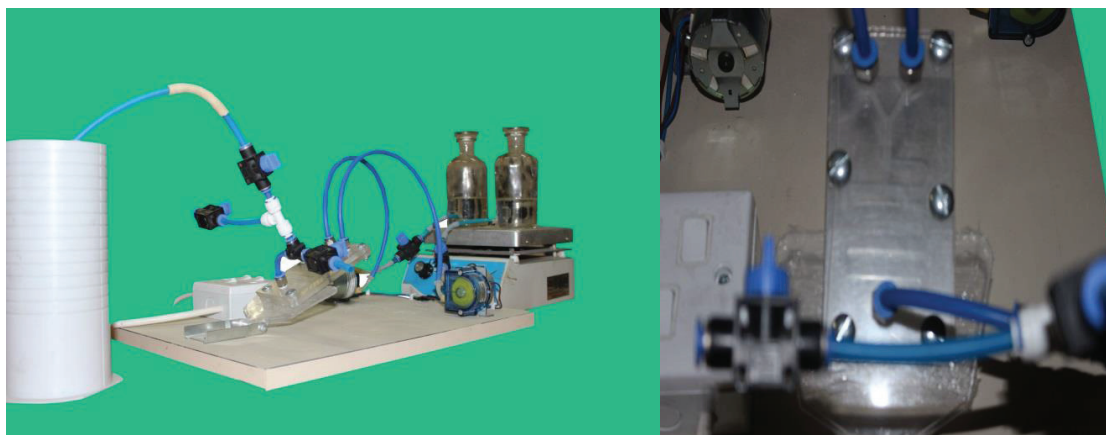


Figure 5 Photographic view of the setup (left) and the microreactor (right)

A solution of certain concentration of dibenzothiophene in hexane was prepared and contained in a 250 ml graduated glass serum container connected to a micropump via a regulating valve. Another 250 ml graduated glass serum container filled with a 30% hydrogen peroxide solution was connected to a second micropump. The two containers were installed on a magnetic stirrer supplied with an electric heater to keep the homogeneity of the mixture in a steady form and heating the feeds to a desired initial temperature. Valves were calibrated with the level in each container so different flow rates could be delivered to the microreactor separately in each run. Each micropump manufactured by Williamson Company Limited, model number 200.015.230.016 was used to deliver the feed (reactants) to the microreactor. Effluent of the microreactor was collected in a graduated 250 ml container surrounded by a cold water bath. Just at the exit of the microreactor the experimental setup was supplied with a valve for instantaneous sampling. The sample was centrifuged to separate water and the upper solution was injected to the HPLC (HPLC–UV; Agilent Technologies 1100; a C-18, (25 cm x 4.6mm i.d.) stainless steel column (packed with Zorbax 8- $\mu$ m, ODS- bound, spherical, silica particles) and was used with a mobile phase consisting of 70% Acetonitrile and 30% Water flowing at a rate of 1ml/min) to find out the unreacted dibenzothiophene concentration in hexane. All containers and tubing outside the microreactor were shielded from UV-exposure. Flowrates of 0.75, 1, 1.5, 2 l/min were used which correlate to 8.1, 6.1, 4, 3min residence times. The fractional degradation ( $x$ ) of DBT was calculated by eqn. 8:

$$\text{Fractional degradation } (x) = (C_o - C(t))/C_o \quad (8)$$

### 2.5 Procedure

To analyze the dibenzothiophene concentration, an HPLC was used in this study. A series of dibenzothiophene/hexan solutions at concentrations of 20, 50, 100, 200, 300, and 500 ppm are used to generate calibration curves. Before



analysis, each solution was diluted by a factor of 1:10; this dilution is done because of the limitations in the HPLC. Similar analytical methods used by others use a mobile phase of Acetonitrile and water, Acetonitrile, Tetrahydrofuran, and water, or Methyl Hydroxide and water (Mezcua, 2007)[25]. In the present work, the mobile phase used was 70:30 Acetonitrile to water ratio with the C-18 column on hand. Figure 6 shows a chromatograph of dibenzothiophene of 400 ppm concentration in hexane with a retention time of 9.93 min. The calibration curve of the dibenzothiophene/hexane solution for area vs. concentration (ppm) is shown in Fig. 7 This curve correlate a given peak area with a known concentration.

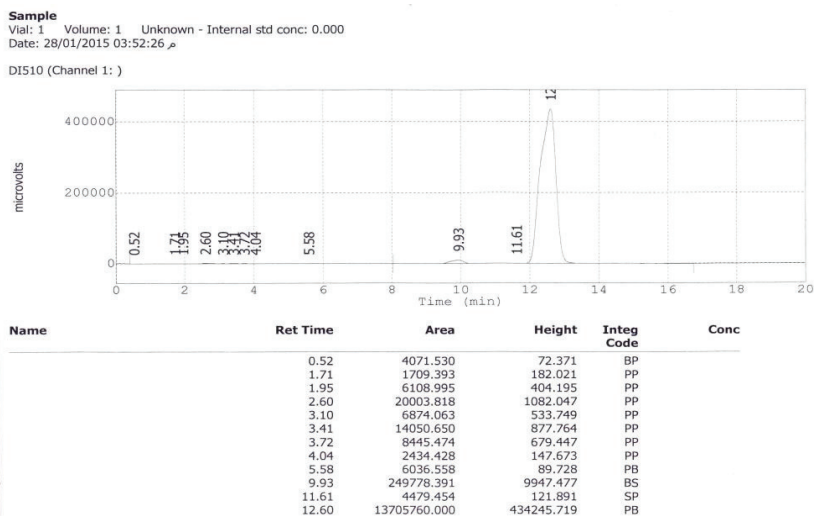


Fig. 6 chromatograph of dibenzothiophene

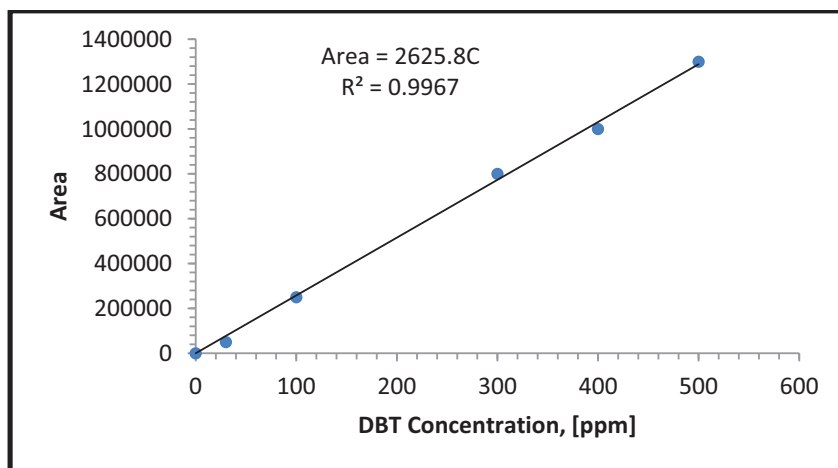


Fig. 7 Calibration curve of dibenzothiophene

## 2. Results and Discussion

### 3.1 Influence of solar incident energy on desulfurization process

To investigate the influence of the incident solar energy on reaction mechanism of DBT, an amount of 500 ppm



of DBT in hexane solution that was used as the feed to the microreactor was mixed with an equal amount of 30% hydrogen peroxide solution and placed in a serum bottle. The bottle is kept at a temperature of 10°C for three hours in a cold water bath. The concentration of DBT in hexane was followed with time as shown in Fig.8. Fig. 8 indicates no apparent change in the concentration of DBT and this revealed that the desulfurization reaction was taking place only inside the microreactor where the materials were illuminated by the UV light. This finding supports and proves that the suggested reaction mechanism that hydrogen peroxide itself does not directly oxidize dibenzothiophene for sulfur removal but it helps the photo excited dibenzothiophene to be oxidized.

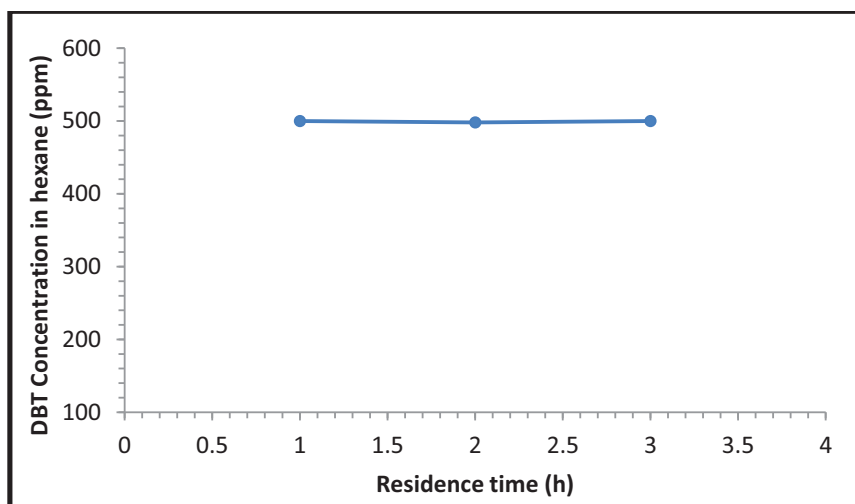


Figure 8 Concentration of DBT in hexane vs. time for a sample of stoichiometric ratio of H<sub>2</sub>O<sub>2</sub>:DBT in a container at 10 °C and C<sub>0</sub>=500 ppm DBT

### 3.2- Influence of concentration of DBT.

Figure 9 represents the experimental results conducted for DBT desulfurization at different space times. Again, it is observed that the outlet concentration decreases as the mean space time inside the microreactor increases. This confirms the fact that if the DBT stays longer in the reactor, its conversion increases as the space time increases. The effect of initial concentration of DBT solution on DBT degradation efficiency has been investigated by varying the DBTs concentration from (100 to 500mg/L). Fig. 9 also plots the variation of DBTs degradation against DBT concentration in the presence of TiO<sub>2</sub>nanoparticles under solar light. As can be seen from Fig. 8 that after 8.1 min of irradiation time the degradation rate was 65%, 58%, and 40% at DBT concentrations of (100, 300, and 500mg/L), respectively. DBT degradation rate was observed to decrease as initial concentration increased.

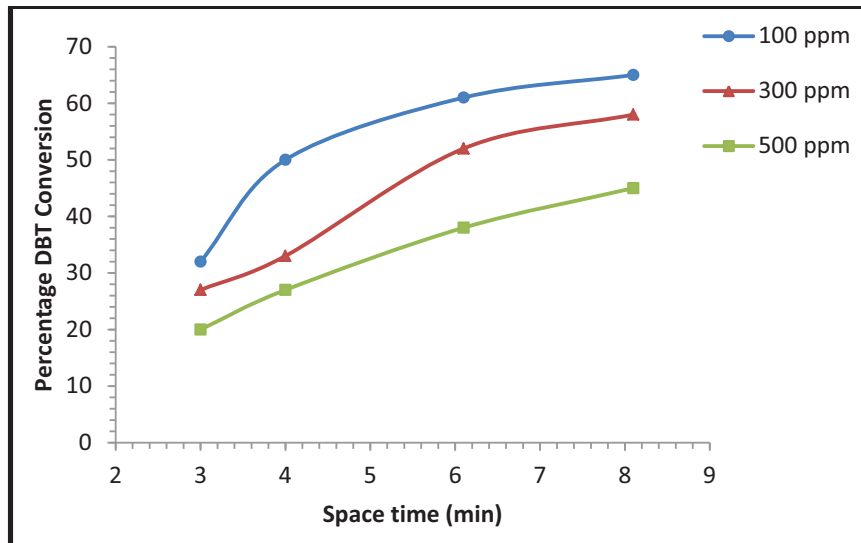


Figure 9 Variation of DBT conversion against residence time at different concentrations of DBT, initial temperature= 50°C, (H<sub>2</sub>O<sub>2</sub>/DBT)=1

### 3.3- Influence of initial temperature and LHSV.

Figure (10) illustrates the effects of reaction temperature and space velocity of the influent stream on the reduction of DBT. An increase in the reaction temperature was observed to result in increased removal of DBT. The effect of temperature was to increase the specific rate constant which pronounced the conversion. As can be seen from Fig. 10, the removal of DBT was shown to decrease markedly as LHSV of the influent stream increased this may be due to the retention time during the oxidation process which was reduced.

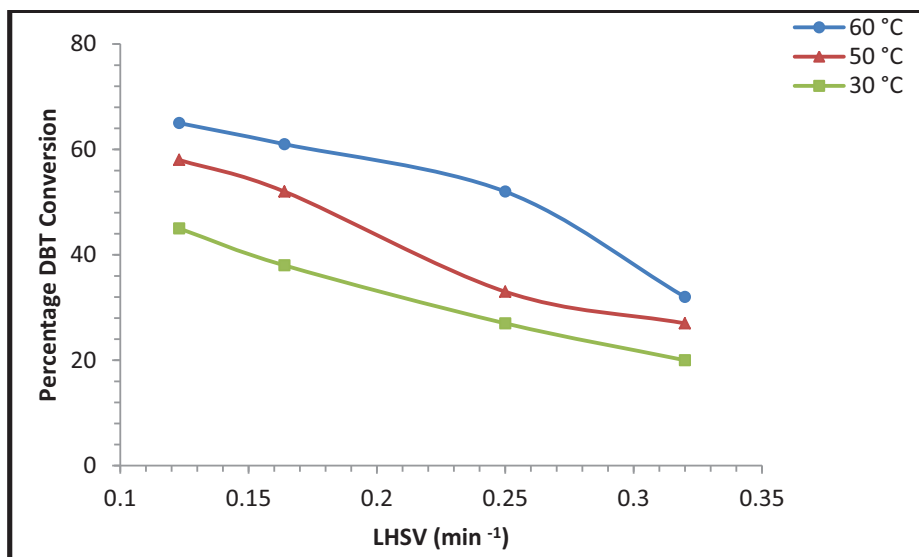
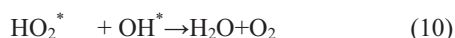
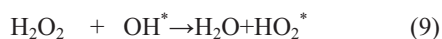


Figure 10 Effect of initial temperature and LHSV on DBT conversion (DBT concentration =100 ppm, (H<sub>2</sub>O<sub>2</sub>/DBT) =1)

### 3.4- Influence of molar ratio of H<sub>2</sub>O<sub>2</sub>/DBT.

Fig. 11 plots the variation of normalized DBT concentration against H<sub>2</sub>O<sub>2</sub>/DBT ratio in solution, keeping all other parameters unchanged. Different H<sub>2</sub>O<sub>2</sub> /DBT/ (1 to 6) was used to study the effect of H<sub>2</sub>O<sub>2</sub> concentration on the desulfurization rate. As can be seen, the removal rate increased with increasing initial concentration of H<sub>2</sub>O<sub>2</sub> at fixed concentration of DBT. The desulfurization rate was slow at low H<sub>2</sub>O<sub>2</sub> concentration, as the formation of hydroxyl radicals was insufficient; this may be explained by the ability of H<sub>2</sub>O<sub>2</sub> to trap the electrons, preventing the electron-hole recombination and hence increasing the chance of formation of OH\* radicals on the surface of the catalyst [26] (Wang and Hong, 1999). However, as the H<sub>2</sub>O<sub>2</sub>/DBT ratio increased beyond a certain limit, (3), the increased decomposition rate became noticeably less. This was because at higher H<sub>2</sub>O<sub>2</sub> concentration, more OH\* radicals were produced leading to a faster oxidation rate. However, these excess free radicals were more prone to react with the excess H<sub>2</sub>O<sub>2</sub> rather than with the DBT [27] (Dixit et al., 2010). One form of this effect can be seen through short-circuiting the semiconductor microelectrode [28] (Akpan and Hameed, 2009), according to eq. (9) and (10):



Therefore, it is imperative to determine the stoichiometric amount of hydrogen peroxide sufficient for complete mineralization. This analysis was not presented in the present work.

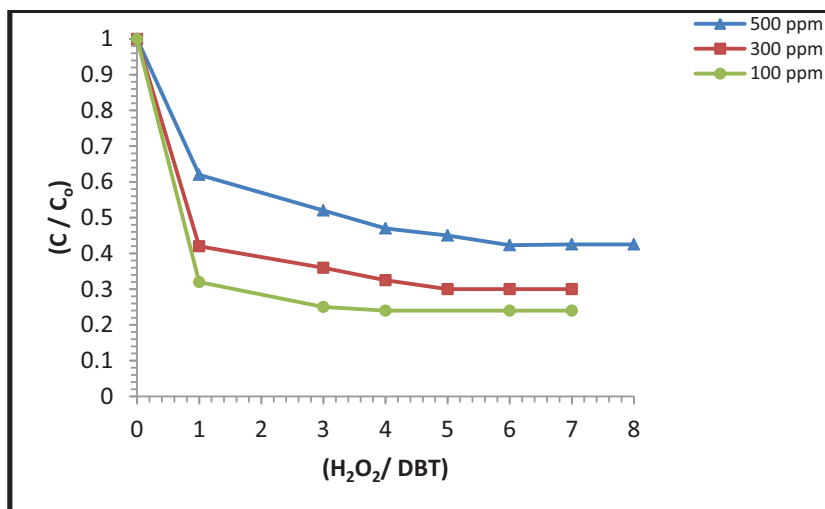


Figure 11 Variation of normalized concentration against (H<sub>2</sub>O<sub>2</sub>/DBT) at different DBT concentrations

### 3. Kinetics study

Kinetics studies were carried out under optimal reaction conditions. The rate constant for the apparent consumption of DBT was obtained from the pseudo first-order eqn 11:

$$r = -dC/dt = kC = k_l C_{AO} (1-x) \quad (11)$$

$$r = C_{AO} dx/dt = k_l C_{AO} (1-x) \quad (12)$$

Eqn 12 can be integrated between  $t=0$  and  $t=t$ , yielding:

$$\ln(1-x) = -k_l t \quad (13)$$

Where  $x$  is the fractional degradation of DBT,  $t$  is the residence time (min),  $k_l$  is the first-order rate constant ( $s^{-1}$ ),  $C_{AO}$  is the initial concentration of DBT, and  $r$  is the reaction rate (mg DBT/cm<sup>3</sup> cat. s).

When  $(-\ln(1-x))$  was plotted against  $t$ , a straight line was fitted to the data of Fig. 12 at 30°C and 50°C with correlation coefficient ( $R^2$ ) of 0.99 and 0.98, respectively. This suggested that DBT photo degradation reaction followed pseudo first-order kinetics. The reaction rate constants were found to be  $1.11 \times 10^{-3} s^{-1}$  and  $1.76 \times 10^{-3} s^{-1}$  at 30°C and 50°C, respectively. However, it is worth to mention that as operating temperature increased above 50°C, a deviation from linearity trend of reaction order is resulted as reported in Table 1. Table 2 lists data related to the results of present work and to the information extracted from published literature.

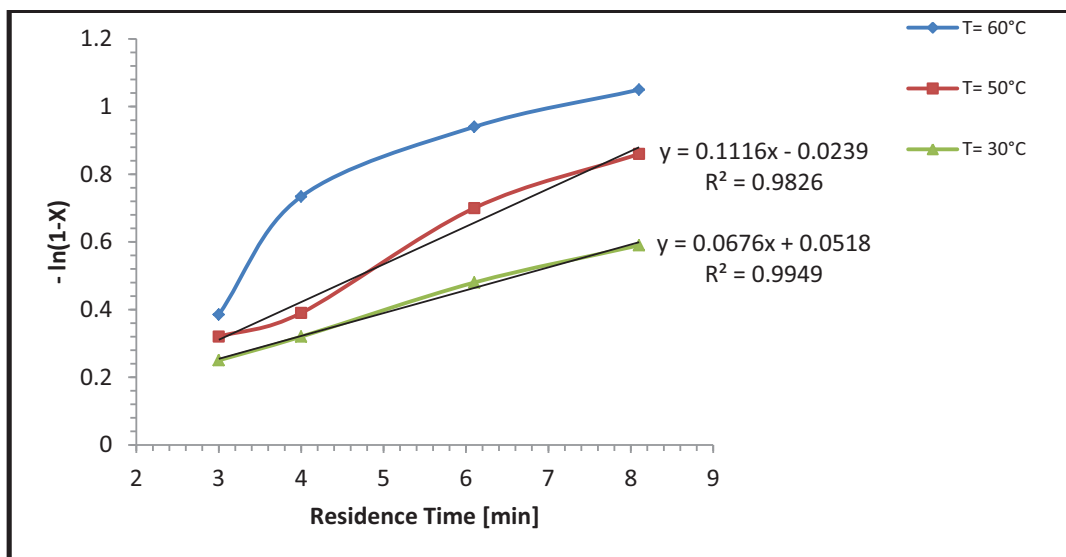


Fig.12  $[-\ln(1-x)]$  against residence time at different temperatures for kinetic study analysis,  $C_{\text{DBT}}=100$  ppm and  $(\text{H}_2\text{O}_2/\text{DBT})=4$

Table 1 Results of kinetic study at  $C_{\text{DBT}}=100$  ppm and  $(\text{H}_2\text{O}_2/\text{DBT})=4$

No.	Temperature ( $^{\circ}\text{C}$ )	Reaction rate law (mg/g-cat.s)
1	30	$1.11 \times 10^{-3} \text{C}$
2	50	$1.76 \times 10^{-3} \text{C}$
3	60	$2.16 \times 10^{-3} \text{C}^{1.15}$

Table 2. Data related to the results of present work and to the information extracted from published literature

Substrate	Desulfurization process	Reaction rate constant	Reactor type	Reference
DBT	Oxidative (30%H <sub>2</sub> O <sub>2</sub> )+ UV lamp	$2.86 \times 10^{-5} \text{ s}^{-1}$	Batch reactor	Shiraishi et al. [29]
DBT	Oxidative (30%H <sub>2</sub> O <sub>2</sub> ) + UV lamp	$1.61 \times 10^{-3} \text{ s}^{-1}$	( liquid cell model SL-3) microreactor	Al-Raie [31]
DBT	Oxidative (30%H <sub>2</sub> O <sub>2</sub> )+ UV lamp	$3.5 \times 10^{-5} \text{ s}^{-1}$	Batch reactor	Hirai et al. [21]
DBT	Solar photocatalysis	$1.17 \times 10^{-3} \text{ s}^{-1}$	Y-shape microreactor	Present work

#### 4. Comparison with Other Researchers' Works

In this section, the results obtained by other researchers for desulfurization of dibenzothiophene are compared with the performance results obtained in the microreactor of the present work. Table 3 summarizes the results obtained by different authors. Curve of ref. [30] shows the profile of dibenzothiophene desulfurization by enzymatic effect of manganese peroxidase (MnP) on a 6 mg/l of DBT in a 100 ml batch reactor operated at 22°C. The degradation profile shows a conversion of 39% achieved after 8 hours of bio-treatment. Curve of ref. [29] shows the concentration profile for dibenzothiophene desulfurization with 30% hydrogen peroxide and solar UV light at  $\lambda > 280 \text{ nm}$  in a batch reactor. A conversion of 82% is achieved after 8 hours of irradiation. The Curve of the present work shows a conversion of 65% achieved after 8.1 minutes of irradiation. It is evident from Table 3 that the microreactor was much more efficient for the desulfurization of dibenzothiophene as was anticipated due to understanding the advantages of microreactors.

Table 3: Comparison between microreactor's performance and performance of batch reactors of ref. [29] and ref.[30]

Substrate	Process	Type of reactor	Retention time, min	Conversion %	Reference
DBT	H <sub>2</sub> O <sub>2</sub> +UV lamp	Batch	480	82	[29]
DBT	Bioprocess	Batch	480	39	[30]
DBT	Solar photocatalysis	Y- shape micreactor	8	65	Present work

#### 5. Conclusion

Desulfurization of dibenzothiophene in the microreactor was investigated in this study. The UV light plays a major role in the desulfurization process and dibenzothiophene. Our experiments show that, in the absence of UV light, no

reaction takes place. Experiments show that the outlet concentration of DBT decreases as the mean residence time in the microreactor increases. This is obvious because dibenzothiophene remain longer in the reactor and thus their conversion increases with time. The reaction rate constant ( $k$ ) was determined and found to be of the order of  $10^{-3} \text{ (s}^{-1}\text{)}$  for dibenzothiophene desulfurization. When this result is compared to reaction rate constants reported by other investigators we find that this reaction proceeds much slower in a batch reactor than in the microreactor. The experimental results obtained from the microreactor study were compared with the work reported by other researchers in this field. We find that the microreactor is much more efficient than batch reactors for the desulfurization process of dibenzothiophene. This is an anticipated outcome based on the understanding of the advantages of microreactors in performing reaction processes in which mass transfer components play important role. In this study the microreactor was capable of achieving a 65% conversion of DBT in approximately 9 (min) which compares to 340-400 (min) for a macroscopic batch reactor operation.

## References

- [1] Fadhil Z. S., Desulfurization of Light Diesel Fuel Using Chloramine T and Polymer Supported Imidation Agent, MSc thesis, Chemical Engineering Department, University of Technology, Baghdad (2010).
- [2] Ting-Mu Chen a, Chih-Ming Wang a, Ikai Wang a, Tseng-Chang Tsai. Promoter effect of vanadia on Co/Mo/Al<sub>2</sub>O<sub>3</sub> catalyst for deep hydrodesulfurization via the hydrogenation reaction pathway. *Journal of Catalysis* 272 (2010) 28–36).
- [3] Al-Malki, A., “Desulfurization of Gasoline and Diesel Fuels, Using Non-Hydrogen Consuming Techniques”, M.Sc. Thesis, King Fahad University of Petroleum and Minerals, October, (2004)-
- [4] Anita Šalić<sup>1</sup>, Ana Tušek<sup>2</sup>, Bruno Zelić<sup>1</sup>, Review: Application of microreactors in medicine and biomedicine, *Journal of Applied Biomedicine*. **10**: 137–153, (2012).
- [5] Rebrov EV, Duinkerke SA, de Croon MHJM, Schouten JC. Optimization of heat transfer characteristics, flow distribution, and reaction processing for a microstructured reactor/heat-exchanger for optimal performance in platinum catalyzed ammonia oxidation. *Chem Eng J*. 93: 201–216, 2003.
- [6] K. Kusakabe, J. of Chem. Eng. of Jpn, Vol. 35, No. 9, pp. 914-917, (2002)
- [7] The aldol reaction of silyl enol ethers within a micro reactor, C. Wiles, P. Watts, S. J. Haswell and E. Pombo-Villar, *Lab on a Chip*, 2001, **1**, 100-101
- [8] Solution phase synthesis of esters within a micro reactor, C. Wiles, P. Watts, S. J. Haswell and E. Pombo-Villar, *Tetrahedron*, 2003, **59**, 10173-10179.
- [9] E. Garcia-Egido, S. Y. F. Wong, B. H. Warrington, A Hantzsch Synthesis of 2-Aminothiazoles Performed in a Microreactor System, *Micro Total Analysis Systems* 2001, ,Proceedings of the  $\mu$ TAS 2001 Symposium, held in Monterey, CA, USA 21–25 October, 2001.p 517-518,Editors: J. Michael Ramsey, Albert van den Berg
- [10] Hideki Amii, Aiichiro Nagaki and Jun-ichi Yoshida, Flow microreactor synthesis in organo-fluorine chemistry, *Beilstein J. Org. Chem.* 2013, **9**, 2793–2802.doi:10.3762/bjoc.9.314
- [11] Matsubara H., Y. Hino, M. Tokizane, and I. Ryu, Microflow Photo-Radical Chlorination of Cyclohexane, *Chemical Engineering Journal*, 2011, 167(2-3); 567-571, DOI:10.1016/j.cej.2010.08.086
- [12] Löwe Holger, Bromination of Thiophene in Micro Reactors, *Letters in Organic Chemistry* , 11/2005; 2(8):767-779, Bentham Science Publishers, DOI: 10.2174/157017805774717517
- [13] Wang Y., editor, and Holladay J. D., editor, *Microreactor Technology and Process Intensification*, ACS



symposium; 914, 2003. ISBN 0-8412-3923-1

[14] Yuan-Chien Tsai, Shung-Jim Yang, Hsun-Tsing Lee, Hsiu-Ping Jen and You-Zung Hsieh, Fabrication of a Flexible and Disposable Microreactor Using a Dry Film Photoresist, *Journal of the Chinese Chemical Society*, 2006, 53, 683-688

[15] Drott J., K. Lindstrom, L. Rosengren, T. Laurell, J. Micromech. Microeng. 7 (1997) 14-23, UK.

[16] Chambers, R. D.; Spink, R. C. H., Microreactors for elemental fluorine, *Chem. Commun* (1999) 883.].

[17] Kelly S., G. Deluga, and W. Smyrl, "Miniature fuel cells fabricated on silicon substrates," *AIChE.*, vol. 48, pp. 1071-1082, 2002]

[18] M. Fujinami, *Micro Total Analysis Systems* 98, pp. 339-342 (1998).

[19] T. Ooi, *Micro Total Analysis Systems* 2002, pp. 121-123 (2002).).

[20] Arantegui, J., Prado, J., Chamorro, E. & Esplugas, S., Kinetics of the UV degradation of atrazine in aqueous solution in the presence of hydrogen peroxide, *J. Photochem. Photobiol. A: Chemistyr*, 88 (1995) 65-74].

[21] T. Hirai, K. Ogawa, Y. Shiraishi, and I. Komasaawa, "Effect of Photosensitizer and Hydrogen Peroxide on Desulfurization of Light Oil by Photochemical Reaction and Liquid-Liquid Extraction", *Ind. Eng. Chem. Res.*, 1997, 36, 530-533].

[22]. Wegeng RW, Call CJ, Drost MK (1996) Proc 1996 Spring National Meeting AIChE, Feb. 25–29 New Orleans, Seiten 1–13

[23]. Branebjerg J, Gravesen P, Krog JP, Nielsen CR (1996), Proc IEEE MEMS '96, San Diego, USA

[24] K.K. Yeong, D. Gobby, P. Angeli, A. Gavrilidis, Z. Cui, Proceedings of the Fourth International Conference on Microreaction Technology, Atlanta, USA, 2000, p. 270.

[25] Mezcuca, Milagros, Amadeo R. Fernandez-Alba, Antonio Rodriguez, Karina Boltes, Pedro Leton, and Eloy Garcia-Calvo. "Chromatographic Methods Applied in the Monitoring of Biodesulfurization Processes-State of the Art." *Talanta* 73 (2007): 103-114].

[26] Wang, Y. & Hong, C.S., "Effect of hydrogen peroxide, periodate and persulfate on photocatalysis of 2-chlorobiphenyl in aqueous TiO<sub>2</sub> suspensions", *Water Res.*, vol. 33, 9, 1999, p.2031-2036 ]

[27] Dixit, A., Mungray, A. K., Chakraborty, M. Photochemical oxidation of phenol and chlorophenol by UV/H<sub>2</sub>O<sub>2</sub>/TiO<sub>2</sub> process: A Kinetic Study. *International Journal of Chemical Engineering and applications*. 1(3) 2010]

[28] U.G. Akpan and B.H. Hameed, Parameters affecting the photocatalytic degradation of dyes using TiO<sub>2</sub>-based photocatalysts: A review, *J. Hazard. Mater.*, 170 (2009) 520–529

[29] Y. Shiraishi, H. Hara, T. Hirai, I. Komasaawa, "A Deep Desulfurization Process for Light Oil by Photosensitizer Oxidation Using a Triplet Photosensitizer and Hydrogen Peroxide in an Oil/Water Two-Phase Liquid-Liquid Extraction System", *Ind. Eng. Chem. Res.*, 1999, 38, 1589-1 595).

[30] Gemma M<sup>a</sup> Eibes González, "Enzymatic degradation of polycyclic aromatic hydrocarbons (PAHs) by manganese peroxidase in reactors containing organic solvents", PhD Dissertation, Chemical Engineering Department, University of Santiago, Spain, 2007

[31] Ali H. Al-Raie, Desulfurization of Thiophene and Dibenzothiophene with Hydrogen Peroxide in a Photochemical Microreactor, MSc thesis, Oregon State University, 2005